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Jen, Gabriel; Stompinis, Nikolaos; Jones, Roderick

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Chloride Ingress in a Belite-Calcium Sulfoaluminate Cement Matrix

Gabriel Jen^a, Nikolaos Stompinis^b, and Roderick Jones^b

^a School of Engineering, University of Aberdeen, AB24 3UE, Scotland UK

^b Concrete Technology Unit, School of Science and Engineering, University of Dundee, DD1 4HN, Scotland UK

Corresponding Author:

Professor Rod Jones

address: Fulton Building H24A, University of Dundee, Scotland DD1 4HN

email: m.r.jones@dundee.ac.uk

phone: +44 (0)1382 388326

Abstract

This paper reports an assessment of the performance of calcium sulfoaluminate-based cementitious materials in chloride-rich environments while addressing the importance that insightful mix proportioning can have on chloride ingress performance. Belite-calcium sulfoaluminate pastes and mortars were prepared at 4 different calcium sulfate to ye'elimite ratios (ranging from 0 to 2) and the properties of the matured matrix (i.e. porosity and binding capacity) were assessed. A comparative assessment was made of the effective chloride diffusion coefficient in belite-calcium sulfoaluminate mortars through commonly used migration (NT Build 492) and diffusion (NT Build 443) accelerated testing protocols. The influence of paste porosity was apparent in NT Build 492, where lower performance was noted for the low sulfate mixes. These results were in contrast with NT Build 443 observations and are attributed to the short testing period of the migration method in which the potential binding affinity of the hydrates is restricted.

Keywords: *sulfoaluminate (D), chloride (D), adsorption (C), diffusion (C)*

1. Introduction

Many contemporary concrete specifications, in addition to the required engineering properties, aim to reduce the embodied energy of the constituent materials, and most commonly replace part of the Portland cement (PC) content with a supplementary cementitious material, typically fly ash or slag. For the vast majority of applications this will continue to be the most cost effective and efficient approach but in some circumstances it may be appropriate to utilise alternative non-Portland cements. This may be for local geological source rock reasons or availability of by-products that can be alkali activated. One of the more extensively used types of non-Portland cements is the family of calcium sulfoaluminate (CSA) cements. These are differentiated from PC by way of their principal phases, ye'elimite (C_4A_3S)/belite (C_2S) as opposed to the alite (C_3S)/belite phases of conventional PC. Although these cements may have a lower embodied CO_2 [1,2] without, at least, equivalent durability, are of little practical use to industry. This paper reports a laboratory study of the issue of resistance of belite-CSA cement-based mixes to chloride ingress with a particular focus on the potential for binding capacity [3,4].

Before deploying CSA cements into aggressive environments it is important to benchmark its likely durability performance. The ability of hydrated CSA cements to generate pore fluids with pH values in excess of the steel passivation threshold has been established by several authors in the literature [5-8]. Less reported is the important aspect of the maintenance of said passivation to ensure attainment of designed service lifespans. Conventionally, PC hydration, particularly when blended with fly ash or GGBS, produces an AFm (monosulfate, $C_4A\$H_{12}$) phase, which can bind chlorides to form Friedel's salt ($C_4ACl_2H_{10}$), which combined with an enhanced microstructure, significantly reduces rates of diffusion [9-11]. CSA/PC blended cement hydration products has been shown to bind chlorides but, in contrast, pure CSA having 16% by weight calcium sulfate (equivalent to a molar ratio of anhydrite to ye'elimite of 1.8) had virtually no ability to bind diffusing chloride ions [12]. As the production of solely AFt (ettringite, $C_6A\$_3H_{32}$) from ye'elimite hydration requires 2 moles of calcium sulfate (CS) for each mole of ye'elimite, it is suggested that the correlation of chloride binding in blended cements is owed to a deficiency of sulfate content in the blend, which alternatively promotes AFm formation. The role of hydration speciation influence might further explain the poor laboratory performance, relative to a reference PC, experienced by a cement mixture over-dosed with calcium sulfate investigated by Kalogridis et al. [13] in which steel mass losses were accelerated in a chloride solution exposed sulfoaluminate matrix. A similar observation has been made by Quillin [14] in 90 day marine exposure testing. Given that it is possible to vary the AFm ratio by varying the calcium sulfate content, it is hypothesised that CSA hydration can be 'tuned' to enhance chloride binding.

2. Materials and Methods

A commercial Grade 72.5 belite-CSA cement containing a high ye'elimite content and no calcium sulfate was sourced from China to be used in this study. Mineral phase and oxide compositions, quantified by X-ray diffraction (XRD) and X-ray fluorescence (XRF) respectively of the CSA cement, are shown in Tables 1 and 2 [15]. A reagent-grade gypsum (C_2H_2) was blended with this cement to generate molar ratios of calcium sulfate to ye'elimite equal to 0, 0.5, 1 and 2 with the aim of controlling the ratio of AFm to AFt hydrates ranging from exclusively AFm to exclusively AFt.

Table 1 Belite-CSA - Mineralogical Composition by XRD with Quantitative Rietveld Refinement [15]

Clinker Phase	wt. %
Ye'elimite ($\text{C}_4\text{A}_3\text{S}$)	53.6
Belite (C_2S)	20.6
Ghelenite (C_2AS)	11.7
Perovskite (CT)	4.8
Merwinite (C_3MS_2)	4.2
Mayenite (C_{12}A_7)	3.3

Table 2 Belite-CSA - Normalised Chemical Composition by XRF [15]

Oxide composition, wt. %						
CaO	Al_2O_3	SiO_2	SO_3	Fe_2O_3	TiO_2	MgO
44.7	32.1	11.0	7.1	2.3	1.5	1.3

To examine the influence of calcium sulfate content on properties of belite-CSA cement matrix, 50mm cement paste cubes were cast using a water to binder ratio of 0.5 (providing enough water for hydration of the ye'elimite and to be compactible), where 'binder' is used to refer to the combined content of belite-CSA cement and any added calcium sulfate, and standard water cured for 28 and 90 days. At each test age, an assessment of paste composition and microstructure was made by stopping hydration through water removal via solvent exchange coupled with drying at 30°C [16]. The extent of hydration was qualitatively measured by peak identification within the XRD patterns of each mixture, using back-loaded samples in order to minimise crystal orientation preference.

74 Additionally, mercury intrusion porosimetry (MIP) measurements were carried out on the 90 day hydrated
75 samples to determine the effect of mixture proportions on pore characteristics [17,18].

76 Chloride binding was measured by chloride sorption [19,20] in the 90 day hydrated paste samples. These were
77 prepared by grinding cured paste blocks until passing a #30 sieve (600um), following which a 10g sub-sample
78 was then immersed in 100mL of sodium chloride with concentrations ranging from 0g/L to 35g/L (equal to
79 average seawater) for 28 days at lab temperature. These were then vacuum filtered to separate the solids and the
80 remaining chloride concentrations were measured by XRF to determine the amount removed by contact with the
81 cement.

82 The resistance of belite-CSA materials to chloride ingress was measured on 28 days water-cured mortar
83 mixtures, having a water to binder ratio of 0.5 (for continuity with the prior investigation) and a sand to binder
84 ratio of 2.75. Two widely used test protocols, i.e. NT Build 492 [21] and NT Build 443 [22], were independently
85 used. The NT Build 492 migration technique is a rapid method of assessing the permeability of concrete to chloride
86 ions by using an electrical charge to accelerate the movement of ions through the test sample. The test specimens
87 were subsequently split and a silver nitrate solution was sprayed on to the freshly broken surfaces. The chloride
88 penetration depth was established as the depth of visible white silver chloride precipitation and the non-steady-
89 state migration coefficient calculated as an average of four tests per each mortar composition investigated. The
90 NT Build 443 chloride diffusion technique differs as uses an increased concentration gradient to expedite chloride
91 ingress. Two disc samples (100 mm diameter, 50 mm thick) were coated with an epoxy membrane such that a
92 single cross-sectional face remained exposed when submerged in a prepared sodium chloride solution (168 g/l) at
93 $20\pm 2^{\circ}\text{C}$ for 180 days. At the end of the immersion period, the chloride diffusion curve of the exposed profile
94 specimens were established by grinding (using a dry process) a series of ten layers at predetermined depths from
95 the exposed surface. The collected powder of each layer was subsequently tested by means of acid digestion,
96 filtration and potentiometric titration, following the procedure described in NT Build 208 [23], to determine the
97 chloride content reported as a percentage by mass of dry mortar powder. The initial chloride content was obtained
98 in the same procedure from an unexposed part of mortar. The calculated chloride diffusion coefficient was
99 determined using a non-linear regression analysis by least squares curve fitting. The first data point (i.e. the surface
100 layer) was discarded and the regression analysis utilised the data set encompassing those values up to a minimum
101 of the chloride content is C_i , the initial chloride content, plus 0.015%.

3. Results

The effect of added gypsum content produced significant differences in the mechanical properties of the mixtures investigated, consistent with prior studies [15,24], with compressive strengths of 28 day cured mortar cubes, shown in Table 3. Inference of the relative contents of AFm and AFt are made using the initial binder compositions of C₃S and C₄A₃S as inputs in the thermodynamic modelling program GEM-Selektor [25,26] with the CEMDATA database [27-29]. The results of this simple method of computation are noted for the absence of any kinetic regulation, however given the rapid hydration rate of C₄A₃S and the consistency of measured XRD spectra below at varied ages, this limitation was acceptable to establish a basic understanding of calcium aluminoferrite (mono-/tri-) sulfate hydrate speciation.

Table 3 Effect of Added Gypsum Content on Inferred Composition and 28-Day Compressive Strength

C ₃ S:C ₄ A ₃ S	Inferred AFm:AFt Ratio, Mass %	Compressive Strength, MPa
0	100:0	60.7
0.5	59:41	48.8
1	33:67	58.4
2	0:100	73.1

The degree of ye'elimite hydration, at both 28 and 90 days, was similar for each of the investigated gypsum contents, as the primary peak corresponding to ye'elimite ($2\theta = 23.72$ degrees) was similarly reduced (Figures 1 and 2). As anticipated, the presence of ettringite ($2\theta = 9.11$ degrees) is more pronounced at increasing gypsum contents, having a seemingly inverse relationship to the presence of stratlingite ($2\theta = 7.13$ degrees). The hydration product calcium aluminium oxide hydrate (CAH₁₀) was only observed for mixes having a lack of added gypsum ($2\theta = 6.24, 12.35$ degrees). The absence of AFm peaks, nominally monosulfate, in the XRD patterns is attributed to poorly formed crystalline structures, but AFm presence is suggested from both the thermodynamic modelling results as well as a mass balance of aluminium present in the system.

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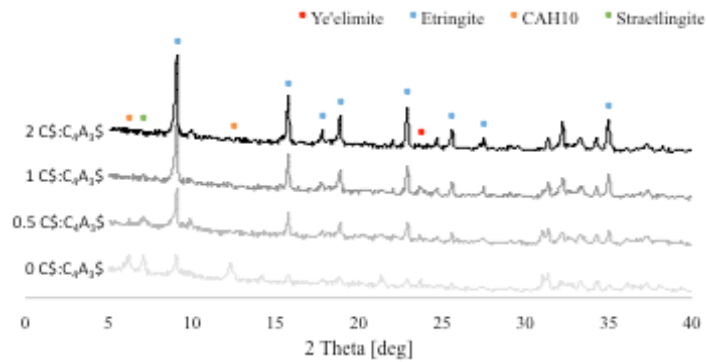


Figure 1 XRD patterns (CuK α radiation) of 28 day hydrated belite-CSA pastes of varied calcium sulfate to ye'elimite ratios

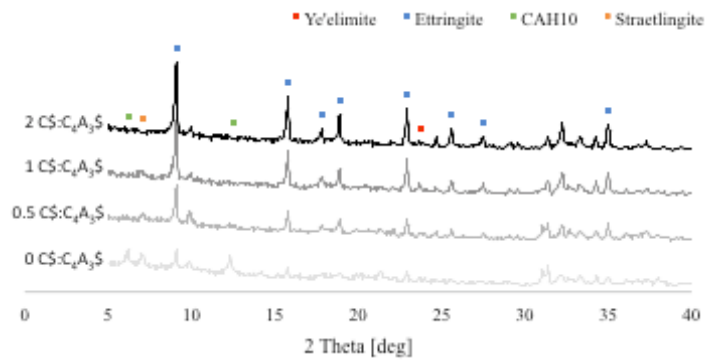


Figure 2 XRD patterns (CuK α radiation) of 90 day hydrated belite-CSA pastes of varied calcium sulfate to ye'elimite ratios

Although porosity, as determined by mercury intrusion porosimetry (MIP), has limitations as measure of in-situ performance [30], it is used here to make comparisons of the relative microstructural characteristics of the test samples. The relative differences in the 90 day results of cement paste MIP analysis were in general agreement with the relative mortar strengths exhibited at an earlier age. Only in a comparison between CS:C₄A₃ molar ratios of 0 and 1 does the typical correlation of low porosity-high strength not hold true, however this was judged to be a product of the significant difference in hydrated phase assemblage (see Figures 1 and 2) and the low density of ettringite. The threshold pore diameter, characterised by Winslow and Diamond [30,31] as a comparative size of “choke points” limiting mercury intrusion, did not follow the same trend. A discontinuity in the connectivity of

141 porosity was observed comparing the two lowest ratios of calcium sulfate (Table 4). Comparatively, the matrix
 142 hydrated with 0 C\$:C₄A₃\$ had the lowest total porosity in a more accessible and open pore network, while
 143 conversely 0.5 C\$:C₄A₃\$ produced more total porosity but with a higher degree of restricted interconnectivity.
 144 Permeability of the CSA matrix being influenced by both total porosity and the interconnectivity of said porosity,
 145 the MIP results would indicate that the highest gypsum addition should produce the most impermeable matrix.

146

147 Table 4 Cumulative Porosity and Threshold Pore Diameter Determined by MIP of Belite-CSA Cement Pastes
 148 Having Varied Calcium Sulfate to Ye'elimite Ratios

Property	C\$:C ₄ A ₃ \$			
	0	0.5	1	2
Cumulative Porosity (%)	20.3	25.1	16.3	13.3
Threshold Pore Diameter (nm)	186.8	48.3	18.2	14.7

149

150 Comparative chloride binding capability is shown in Figure 3. The difference of chlorides in solution between
 151 the original solution and the content remaining after 28 days of paste immersion is normalised to determine the
 152 binding capacity of a 100g paste sample. As a point of reference, using the aforementioned water to binder ratio
 153 of 0.5 and the belite-CSA cement oxide compositions of Table 2, the Al₂O₃ contents of 100g of belite-CSA cement
 154 paste having molar ratios of 0, 0.5, 1 and 2 C\$:C₄A₃\$ can be calculated as 21.4, 19.5, 17.8 and 15.9g respectively;
 155 this range being a reflection of the effect of calcium sulfate dilution. With the mass ratio of Cl₂:Al₂O₃ in Friedel's
 156 salt being roughly 0.7, full utilisation of all available alumina in conversion to chloride-bound Friedel's salt would
 157 not allow for more than 11-15g Cl⁻ to be bound. For the belite-CSA cement having no added calcium sulfate, the
 158 highest content of bound Cl⁻ measured at the maximum considered solution concentration, 21.2g Cl/L, is equal
 159 to 13.3g (of a possible 14.9g), which shows that there is significant exploitation of alumina to maximise chloride
 160 binding performance. Similar efficiency is not noted for the highest calcium sulfate cement blend in which the
 161 greatest value of bound Cl⁻, 5.5g, compares unfavourably with the theoretical limit of 11.1g.

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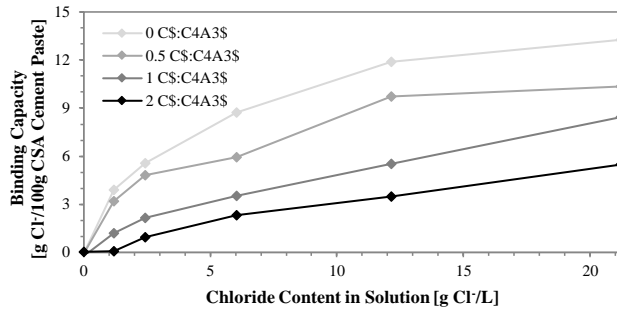


Figure 3 Chloride binding of belite-CSA pastes having varied calcium sulfate to ye'elimite molar ratios

Rapid chloride penetration testing (RCPT), using the migration-induced accelerated protocol of NT Build 492, showed a reverse trend after 24 hours of applied test voltages (Table 5). Chloride ingress was measured using silver nitrate staining and the corresponding calculated non-steady-state migration coefficients (D_{nssm}) indicated that the mortars fabricated with high C:S:C₄A₃ ratios, greater than 1, had the highest resistance to chloride ingress. It was noted that for the 0.5 C:S:C₄A₃ ratio mixture, the standard test voltage (30V) produced a higher flowing current than is advised in the standard and thus for this sample, the applied voltage was lowered to 25V. The reason for this is that the 0.5 C:S:C₄A₃ ratio mixture had the highest porosity (Table 4). The largest non-steady-state migration coefficient was measured in the 0 C:S:C₄A₃ ratio mixture although the validity of this measurement is questionable and is discussed further below.

Table 5 Non-Steady-State Migration Coefficients of belite-CSA Mortars Having Varied Calcium Sulfate to Ye'elimite Ratios

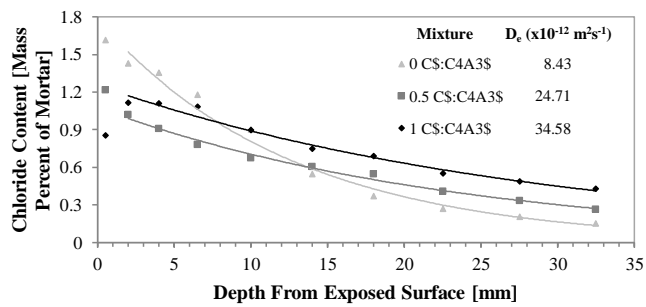
Test parameters	C:S:C ₄ A ₃			
	0	0.5	1	2
Test Voltage (V)	30	25	30	30
Duration (Hrs)	24	24	24	24
D_{nssm} ($\times 10^{-12}$ m ² s ⁻¹)	6.86	3.70	2.47	2.80

While the amounts of crystalline AFm hydrates are not readily apparent from the XRD spectra, shown in Figures 1 and 2, it can be inferred that the balance of reacted ye'elimite that does not go towards forming ettringite

181 is likely to be contributing to the AFm content, as suggested by thermodynamic modelling [32]. An approximation
 182 of the AFm content can, therefore, be made from the ettringite content. Using a C₃S:C₄A₃S ratio of 2, the ettringite
 183 intensity for any other calcium sulfate addition rate, taking into account the dilution effects of calcium sulfate, is
 184 inversely proportioned to the quantity of chloride binding hydrates.

185 To assess this, additional long-term testing was carried out by imposing a 165 g/L sodium chloride
 186 concentration gradient upon 100 mm diameter by 50 mm long cylinder mortar samples. Elongated test durations,
 187 6 months, were chosen over the prescribed 35 days due to the low chloride ingress rates of these test samples.
 188 Further, due to the similarity noted in porosity measurements (Table 4) and RCPT performance (Table 5) between
 189 the 1 and 2 C₃S:C₄A₃S ratio mixtures, the 1 C₃S:C₄A₃S ratio mixture was subjected to this longer test protocol and
 190 assumed to be a fair representation of the potential performance of the 2 C₃S:C₄A₃S ratio mixture. After 6 months,
 191 acid-soluble chloride contents were measured, which does include the ions present in the pore volume as well as
 192 bound within hydrate species, and then normalised by mortar masses having equivalent cementitious paste
 193 content. The results, with curve-fitted effective transport coefficients (D_e), are given in Figure 4 and show the
 194 relative performance in contrast to the data given in Table 5. Specifically addressing the profile shape of chloride
 195 content, the shallow slopes of the 0.5 and 1 C₃S:C₄A₃S ratio mixtures represent significant ion mobility achieved
 196 towards equilibrating the concentration gradient of chloride ions. In contrast, the 0 C₃S:C₄A₃S ratio mixture is
 197 noted for the steepened slope noted from the surface to a depth of 30 mm depicting a restricted movement of ions
 198 once entering the cement matrix. As porosity measurements (Table 4) do not exhibit a correlated difference, the
 199 reason for this is due to chloride binding.

200



201

202 Figure 4 Chloride profiles of belite-CSA mortars with varied calcium sulfate to ye'elimite ratios

203

4. Discussion

The amount of calcium sulfate used to 'activate' CSA cement has a significant effect on the AFm/AFt ratio. The dosage rates under consideration here are, by virtue of being multiplicative factors of the high ye'elimite content of the CSA cement, numerically high. For example, at a molar ratio of 2, the blended gypsum comprises roughly one quarter of binder mass. This is noted because even at the lower calcium sulfate addition rates, crystalline ettringite stability remains high, persisting at 90 days as a predominant phase. A similar stability is not typically associated with the initially formed ettringite of PC, where low sulfate mixtures, conventionally with respect to tricalcium aluminate (C_3A), experience a conversion of ettringite to monosulfate until the accessible alumina clinker phases are depleted. While sulfation of PC is optimised around limiting the rate of C_3A hydration, this is not required for CSA cements. Thus, the sulfate addition level can be user designed to optimise either setting time, strength, porosity or hydrated phases depending on the performance requirements for specific applications. The metastability typically associated with ettringite appears steadied by the internal chemistry of CSA cement in which pore solution sulfate levels may experience buffering by other clinker and hydrate phases, with auxiliary alumina equilibrated by stratlingite ($C_2AS \cdot H_8$) formation.

The data presented here demonstrate the interplay of chemistry-controlled preference of calcium sulfoaluminate hydrate phase and the chloride-binding capacity of CSA cements has a critical role in shaping the overall performance of CSA cement with respect to chloride ingress. This is not necessarily a heretofore unexpected phenomenon, as indeed Galan and Glasser [33] suggest as much in their review and assessment of cement paste-chloride interactions and proposed calculation of maximum binding capacity in PC. Herein, the difference expressed is that the phase assemblage into which aluminates are hydrated plays a critical role in the low range of chlorides prevalent along the initial front of chloride ingress, as evident in the correlation noted on the low concentration end of Figure 3. Only in more concentrated solutions, at which point ettringite stability degrades, does the phase-independent role of alumina content come to the fore. In Figure 3, this can be observed at higher solution concentrations where even paste compositions with high ettringite contents develop notable chloride-binding capacity.

The results also highlight an important distinction between the different test methodologies used for determining apparent diffusion coefficients. The data arising from the short duration, migration-accelerated methodology of NT Build 492 shows that for high sulfate mixtures, pore refinement is the property controlling ion mobility. These results and the associated interpretation is in agreement with Ioannou et al. [34], who promoted improved chloride diffusion resistance owing to microstructural densification via preferred ettringite formation in

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a ternary calcium sulfoaluminate-anhydrite-fly ash cement. However, the long duration result, using the concentration-accelerated methodology of NT Build 443, suggests that the restriction of chloride ion ingress is via hydrate conversion and binding. This has significant impact on the selection of standard test methods to characterise the real world durability performance of CSA concrete. There is a need to achieve test results in as rapid a manner as possible but short duration testing suppresses the impact of kinetic-controlled conversion that might otherwise provide an effective barrier to ion transport. For CSA based mixes, the degree of acceleration in test protocols introduces erroneous performance, which is certainly not a heretofore un-encountered phenomenon in the field of concrete testing. Yet, for CSA and other high binding capacity cement combinations, test methods that include a sufficiently long test period that allows chloride ions to be bound to hydrates are necessary to achieve representative inputs for service life estimation. This is not to say that the elevated concentrations of chloride solution experienced in the alternative method are without consequence. Rather, it highlights that there is a present need to collect data to ensure that there is a sufficiently accurate correlation with field results, as exists for PC.

Conventionally, a strong association is placed between concrete strength/porosity and chloride resistance. For PC mixtures having a restricted range of compositions, this association is easy to understand as a stronger, less porous mixture has a more restricted network of pathways to allow for permeation of ions. Importantly, the data arising from this project shows that transferring these assumptions to CSA cement may introduce a systemic error depending upon the method chosen to establish diffusion coefficients. Rather, strength and porosity/threshold pore diameter in the range of CSA cement paste under investigation are shown to have marginal correlation, and present no unifying trend when compared with associated chloride diffusion rates, taking into account both methods of testing. Nominally, the best overall performance was observed with the 0 CS:C₄A₃ ratio mixture as it is quantifiably better than the added sulfate mixtures, when examined through the concentration-accelerated NT Build 443 method. It is argued that this reflects the advantage of obtainable variety of hydrate compositions achievable based upon the specifiers choice of calcium sulfate additive content. Inherently, this implies an optimisable product having significant aptitude for utilisation by the concrete construction industry when presented with corrosion susceptible environments, although in this study it was not possible to determine whether this would be better than an equivalent fly and/or slag modified PC concrete.

5. Conclusions

The research data presented was aimed at determining whether CSA hydrates could be manipulated by control of the calcium sulfate content available during hydration for the purpose of enhancing and optimising the material's resistance to chloride ingress. The chloride test results presented here are representative of testing conducted on a limited number of samples of each mix type tested for each condition assessed. The limitations with respect to the conclusions based upon a small number of data points are recognised, however the performance discussed herein is sufficient to raise concerns over testing methodology when using these alternative cement mixtures.

The primary conclusions of this work are:

- Ettringite persistence in added calcium sulfate/belite-CSA binders is perhaps higher than customarily appreciated in PC and depletion of calcium sulfate is not observed to initiate a conversion of already formed ettringite to monosulfate within the time scale investigated. Therefore, the amount of added calcium sulfate can be used to change the ratio of AFm/AFt hydrates in mature cement paste.
- At low chloride concentrations, binding of low sulfate (0 and 0.5 C₃S:C₄A₃S) belite-CSA pastes are comparable, while high sulfate (1 and 2 C₃S:C₄A₃S) belite-CSA pastes exhibited negligible binding potential.
- At high chloride concentrations (equivalent to normal seawater) binding capacity was found to be inversely proportional to the total calcium sulfate content.
- The comparative resistance to chloride ingress of CSA mixes should be determined using test methods of sufficiently long duration to allow binding to form. In this case, a test duration of 6 months was used, which on a practical basis might be too long for industrial deployment. However, rapid testing was found to be unrepresentative, if highly conservative.

Further work will be necessary to produce accurate shorter term testing and whatever method, establishing the relationship of paste porosimetry and mortar strengths as a predictive basis of chloride ingress performance will be required, with validation ultimately from field data. Furthermore, while this study has focused upon a single durability issue, i.e. chloride ingress, an assessment of the carbonation potential of CSA based cements will be necessary to ensuring long term steel passivation stability where structures are not fully saturated and binding is compromised by the resulting lower pore alkalinity. It should also be noted that varying the calcium sulfate does influence the strength properties of CSA cement-based materials and it is likely that the optimum for chloride resistance would not be coincident for strength.

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296

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